

CRYSTAL STRUCTURES AND MINERAL CHEMISTRY OF  
HYDRATED FERRIC SULFATES. I. THE CRYSTAL  
STRUCTURE OF COQUIMBITEJ. H. FANG AND PAUL D. ROBINSON, *Department of Geology,  
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## ABSTRACT

Coquimbite,  $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , is hexagonal, space group  $P\bar{3}1c$  with  $a = 10.922 \text{ \AA}$ ,  $c = 17.084 \text{ \AA}$  and  $Z = 4$ . The structure was partially solved by the Patterson method which yielded most of the heavy atom positions. The remaining atoms were then located by several cycles of Fourier synthesis. The dominant structural feature is a discontinuous chain, composed of alternating Fe octahedra and S tetrahedra, parallel to, and approximately one-half the length of, the  $c$  axis. The symmetry causes the chain to be repeated in the upper one-half of the cell. The individual chain segments are linked through hydrogen bonds only. The geometrical arrangement of the chains gives rise to "channels," paralleling the  $a_1$  and  $a_2$  axes, which are occupied by water molecules linked to the chains by hydrogen bonds. The (2b) equipoint is occupied almost totally by  $\text{Al}^{3+}$  substituting for  $\text{Fe}^{3+}$ . Average cation-oxygen distances are: S-O = 1.474  $\text{ \AA}$ , Fe(1)-O = 2.006  $\text{ \AA}$ , Fe(2)-O = 1.990  $\text{ \AA}$  and  $(\text{Al}_{90}, \text{Fe}_{10})\text{-O} = 1.889 \text{ \AA}$ . The final isotropic  $R$ -factor, with 420 reflections, is 6.1%.

## INTRODUCTION

The mineral group with the general formula  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  is composed of lausenite ( $6\text{H}_2\text{O}$ ), kornelite ( $7\text{H}_2\text{O}$ ), coquimbite ( $9\text{H}_2\text{O}$ ), para-coquimbite ( $9\text{H}_2\text{O}$ ) and quenstedtite ( $10\text{H}_2\text{O}$ ) (Palache, *et al.*, 1951). By solving the structure of each of these minerals we hope to be able to describe, in detail, their dehydration mechanisms and to explain the polymorphic relationship which exists between coquimbite and para-coquimbite. Coquimbite was chosen to be the first of this series of papers. Its formula should be written as  $(\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O})$  because there is often an Al-for-Fe substitution (Palache, *et al.*, 1951).

## EXPERIMENTAL

The crystals of coquimbite, from Tierra Amarilla, Chile, were kindly supplied by the U. S. National Museum, Smithsonian Catalog No. 12548. Precession photographs and measurements with a Buerger single-crystal diffractometer yielded the following unit cell information:  $a = 10.922 \pm .009 \text{ \AA}$ ,  $c = 17.084 \pm .014 \text{ \AA}$ , space group =  $P\bar{3}1c$  and  $Z = 4$ . Optically, our specimen is uniaxial (+) with  $\omega = 1.539 \pm .002$  and  $\epsilon = 1.548 \pm .002$ .

An 0.35 mm diameter sphere was used for data collection and a total of 428 observable, nonequivalent reflections were collected using a Buerger automated diffractometer and Mn-filtered Fe radiation. A reflection was considered observed if:  $I - B \geq 3.0 \sqrt{I + B}$  where  $I$  = total counts accumulated during the scan and  $B$  = background. Standard reflections were carefully monitored to insure system stability. The data were corrected for Lp and absorption. For a more detailed explanation of procedures used during the data collection and reduction stages, see Robinson and Fang (1969).

## DETERMINATION OF THE STRUCTURE

Initially, we attempted to solve the structure by use of the  $\Sigma_2$  function. However, no

meaningful structure could be deduced. We then resorted to the Patterson method and we were able to extract indications of the heavy atom positions. By use of this information and a combination of numerous Fourier syntheses and a bit of trial and error, all of the atomic positions were eventually found. A structure factor calculation, using the original atomic coordinates from the Fourier maps, gave an *R*-factor of 24 percent.

## REFINEMENT

Several cycles of full matrix least-squares refinement using all of the 428 observable reflections, while varying the scaling factor and the atomic parameters, lowered the *R*-factor to 18 percent. Form factors were obtained from the International Tables for X-ray Crystallography (1962). All parameters were then varied and the *R*-factor dropped to 9 percent but was meaningless since many temperature factors became negative. In contrast, the temperature factor of the cation at the (2b) equipoint was very high. Bond-length calculations, performed at this point, showed that the average cation-oxygen distance for the octahedrally coordinated cation at (2b) was much shorter (1.89 Å) than the average Fe-O distances for the other two Fe octahedra (2.01 Å and 1.99 Å). Coupled with this, a difference Fourier map showed a large hole at the (2b) site. Therefore, in the next stage of refinement, Al was substituted for Fe at the (2b) position. The result was striking. The *R*-index dropped from 18 percent to 12 percent and all of the temperature factors, with the exception of *S*, were quite acceptable. In the next refinement stage, a weighting scheme previously used by us (Robinson and Fang, 1969) was employed which rectified the situation while lowering *R* to 6.6 percent. After removal of 8 strong, low angle reflections which were obviously suffering from secondary extinction, final isotropic refinement was conducted, varying all parameters including the Al:Fe ratio in the (2b) site. The final isotropic *R*-factor is 6.1 percent with a final Al:Fe ratio of 90:10 at (2b).

In order to check the accuracy of our Al:Fe site refinement, a wet chemical analysis of our coquimbite sample was obtained. The chemical analysis yielded an Al:Fe atomic ratio of 1.00:3.41, within 1 percent of the predicted ratio of 1.00:3.44 based on the results of our X-ray refinement.

Atomic coordinates and temperature factors are given in Table 1. The observed and

TABLE 1. ATOMIC COORDINATES, TEMPERATURE FACTORS AND STANDARD ERRORS<sup>a</sup>

Atom	Equipoint	<i>x</i>	<i>y</i>	<i>z</i>	$\beta(\text{\AA}^2)$
(Al <sub>90</sub> , Fe <sub>10</sub> )	2b	0	0	0	1.07(14)
Fe(1)	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1.71(10)
Fe(2)	4f	$\frac{2}{3}$	$\frac{1}{3}$	.0025(1)	2.19(9)
S	12i	.2444(2)	.4146(2)	.1232(1)	0.49(7)
O(1)	12i	.3187(7)	.3451(7)	.0909(4)	1.42(14)
O(2)	12i	.1081(7)	.3106(7)	.1548(4)	1.03(14)
O(3)	12i	.2197(7)	.4946(7)	.0597(4)	1.21(14)
O(4)	12i	.3349(7)	.5158(6)	.1838(3)	0.74(13)
Ow(1)	12i	.1645(7)	.0698(7)	.0622(4)	1.18(14)
Ow(2)	12i	.4485(7)	.1153(7)	.2101(4)	1.71(16)
Ow(3)	12i	.5720(8)	.1616(8)	.0720(4)	1.70(15)

<sup>a</sup> In parentheses.

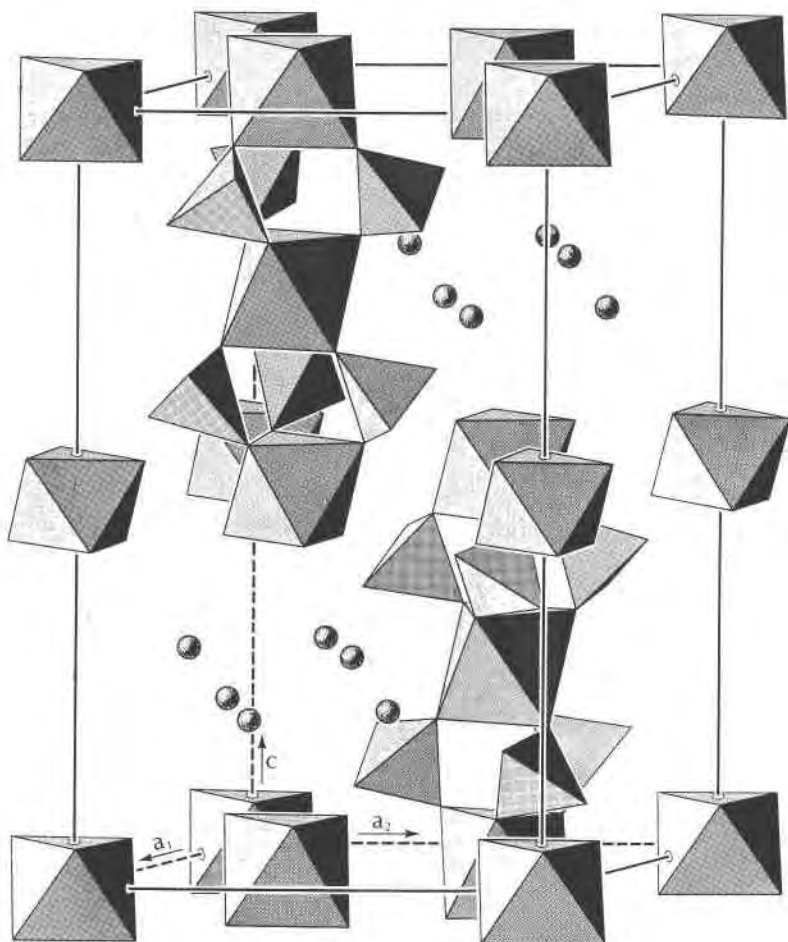


FIG. 1. Polyhedral representation of the coquimbite structure.

calculated structure factors are listed in Table 2 which has been deposited with the American Society for Information Science, The National Auxiliary Publications Service.<sup>1</sup>

#### DISCUSSION OF THE STRUCTURE

The three outstanding features of the coquimbite structure can be easily seen in Figure 1. They are: (1) Clusters of six  $\text{SO}_4$  tetrahedra and three Fe octahedra which share only corners. There are two centrosym-

<sup>1</sup> Order NAPS Document No. 01111 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, N. Y. 10022; remitting \$2.00 for microfiche or \$5.00 for photocopies, in advance payable to CCMIC-NAPS.

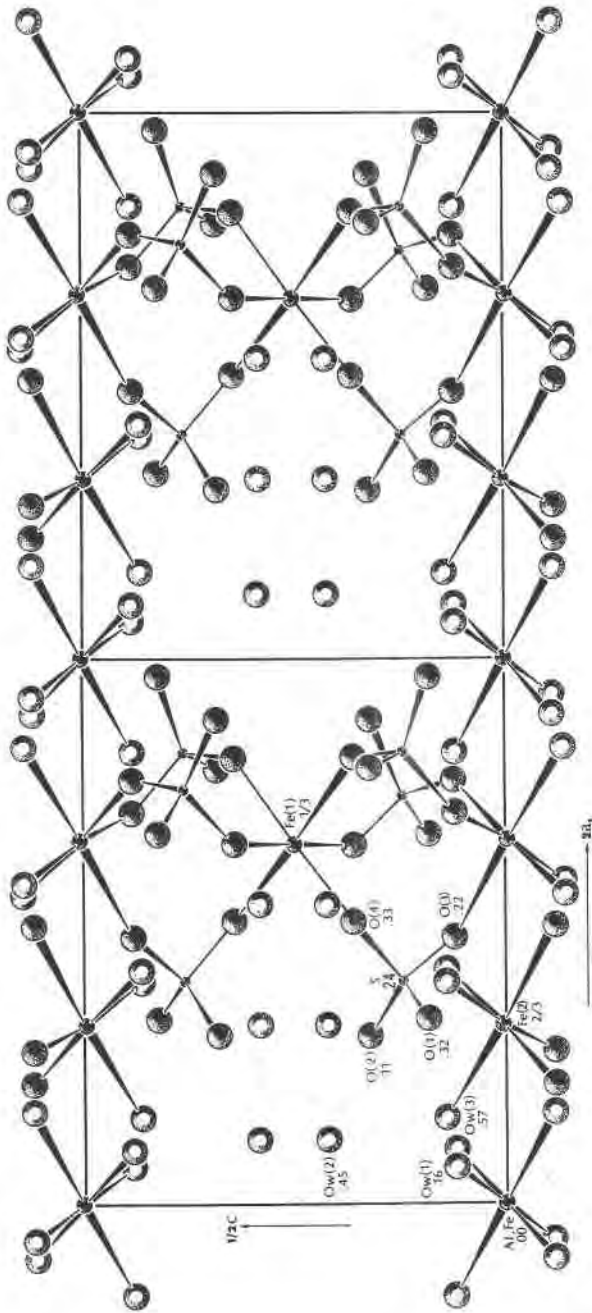


Fig. 2. The crystal structure of coquimbite projected on (100). Numbers indicate fractional atomic heights along  $a_1$ . Spheres with hollow centers denote Ow atoms.

TABLE 3. SELECTED INTERATOMIC DISTANCES AND ANGLES FOR COQUIMBITE<sup>a</sup>

Tetrahedral coordination around S			
S-O(1)	1.469(9) Å	O(1)-O(2)	2.400(11) Å
-O(2)	1.451(8)	O(1)-O(3)	2.426(12)
-O(3)	1.500(8)	O(1)-O(4)	2.387(10)
-O(4)	1.476(7)	O(2)-O(3)	2.391(10)
		O(2)-O(4)	2.419(10)
		O(3)-O(4)	2.418(10)
Mean	1.474 Å	Mean	2.407 Å
			Mean
			110.6(5)°
			109.6(4)
			108.3(4)
			108.2(4)
			111.5(4)
			108.7(4)
			109.5°
Octahedral coordination around Fe(1), Fe(2) and (Al, Fe)			
Fe(1) Octahedron		Fe(2) Octahedron	
Fe(1)-O(4)	2.006(7) Å [×6]	Fe(2)-O(3)	1.967(8) Å [×3]
		Fe(2)-Ow(3)	2.014(8) Å [×3]
Mean	2.006 Å	Mean	1.990 Å
O(4)-O(4)	2.869(14) Å [×6]	O(3)-O(3)	2.867(11) Å [×3]
O(4)-O(4)	2.788(14) Å [×3]	O(3)-Ow(3)	2.890(11) Å [×3]
O(4)-O(4)	2.819(14) Å [×3]	Ow(3)-O(3)	2.683(11) Å [×3]
		Ow(3)-Ow(3)	2.819(11) Å [×3]
Mean	2.836 Å	Mean	2.815 Å
O(4)-Fe(1)-O(4)	91.3(4)° [×6]	O(3)-Fe(2)-O(3)	93.6(4)° [×3]
O(4)-O(4)	88.1(4)° [×3]	O(3)-Ow(3)	93.1(4)° [×3]
O(4)-O(4)	89.3(4)° [×3]	Ow(3)-O(3)	84.7(4)° [×3]
		Ow(3)-Ow(3)	88.8(4)° [×3]
Mean	90.0°	Mean	90.0°
			Mean
			1.889(8) Å [×6]
			1.889 Å
			2.705(14) Å [×6]
			2.638(13) Å [×6]
			2.672 Å
			88.6(3)° [×6]
			91.4(3)° [×6]
			90.0°

<sup>a</sup> Standard deviations in parentheses.

metrically related clusters in each unit cell, giving rise to what may be described as a discontinuous, zig-zag chain of S-tetrahedra and Fe octahedra parallel to the  $c$  axis. Each individual cluster is linked to the next through H-bonds; (2) The geometrical arrangement of the chains gives rise to "channels" paralleling the  $a_1$  and  $a_2$  axes which are filled by  $H_2O$  molecules. This feature can also be clearly seen in the (100) projection (Fig. 2); (3) The independent octahedra located at the origin and at the center of the  $c$  edges. This is the  $(Al_{90}, Fe_{10})$  octahedron previously discussed.

The hydrogen bond system seems to be rather complicated and Fourier difference maps did not allow us to choose among the numerous geometrical possibilities.

Table 3 lists interatomic distances and angles for coquimbite. The mean S-O distance in the sulfate tetrahedron is 1.474 Å, in excellent agreement with those found in other sulfate hydrates. An interesting feature is the lengthening of the S-O distance when the oxygen atom is also linked to an Fe atom. In the present structure, O(3) and O(4) are shared by two different Fe octahedra and the S-O(3) and S-O(4) distances are longer than the two oxygens which are bounded only to S. This phenomenon has also been found in krausite (Graeber, *et al.*, 1965), amarantite (Susse, 1968) and roemerite (Fanfani, *et al.*, 1970) and is explainable in terms of  $\pi$ -bonding due to a decrease of negative charge on the oxygen atoms.

The mean Fe(1)-O distance is 2.006 Å and the octahedron is quite regular. The Fe(2) atom is surrounded by 3 oxygen atoms and three  $H_2O$  molecules with an average Fe-O distance of 1.990 Å. This octahedron shows the largest angular deviation.

The  $(Al_{90}, Fe_{10})$  octahedron is surrounded by six  $H_2O$  molecules, the average  $(Al_{90}, Fe_{10})$ - $H_2O$  distance being 1.889 Å. It is interesting to compare this value with the average Al- $H_2O$  distance of 1.883 Å found in tamarugite (Robinson and Fang, 1969).

#### ACKNOWLEDGEMENTS

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